Nucleation in Hard Spheres Systems

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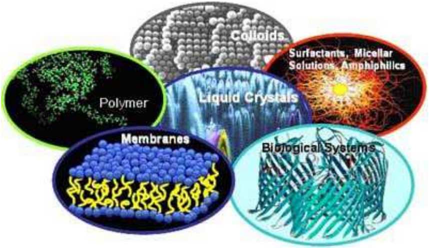
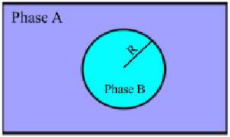
Softmatter

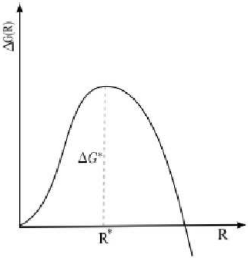


They include liquids, colloids, polymers, foams, gels, granular materials, and a number of biological materials.
The energy scale comparable with room temperature thermal energy.

Illustration taken from SoftComp website

Classical Nucleation Theory





$$\Delta G = 4\pi\gamma R^2 + \frac{4\pi\Delta\mu\rho}{3}R^3 \qquad R^* = \frac{2\gamma}{\rho|\Delta\mu|}$$

$$\Delta G_{crit} = \frac{16\pi\gamma^3}{3(\rho|\Delta\mu|)^2} \qquad I = \kappa \exp\left[-\frac{16\pi\gamma^3}{3(k_B T\rho|\Delta\mu|)^2}\right]$$

source Hamed Maleki, PhD Thesis, University of Mainz, 2011

Hard Spheres

$$V(r) = \begin{cases} \infty & \text{if } r < R \\ 0 & \text{if } r \geq R \end{cases}$$

collisions
are elastic $\Rightarrow$ internal energy constant

$$F = -TS$$

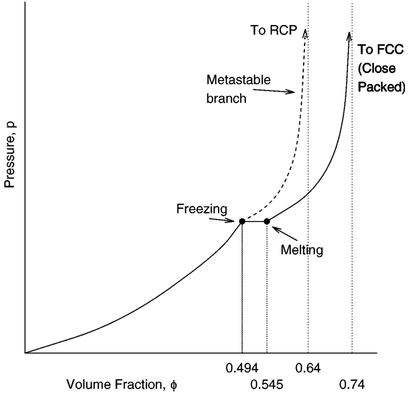
most simple model for a liquid

$$\eta = \frac{1}{6}\pi R^3 \rho$$

The equations of state is given by

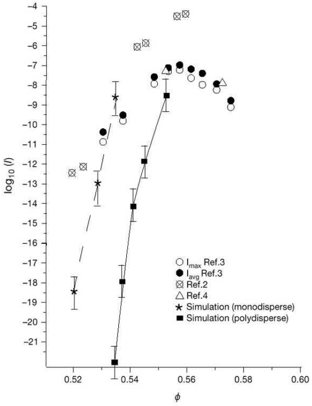
$$\frac{\beta P}{\rho} = \frac{(1+\eta+\eta^2)}{(1-\eta)^3}$$

Phasediagram for Hard Spheres



Rintoul, Md. and Torquato, S., 1996, PRL 77, 20, 4198-4201.

Rare event Sampling

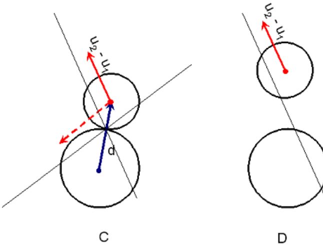


Stefan Auer and Daan Frenkel, Nature 409, 1020-1023 (2001)

Motivation Event driven molecular dynamics

time driven MD simulation vs. event driven MD simulation

V is a discontinuous potential
⇒ free flight in between collisions
NVE ensemble
T is trivial parameter
setting the time scale, i.e. diffusion constant



Alder, B. J., and Wainwright, T. E., 1957, J. chem. Phys., 27, 1208.

Algorithm Event driven molecular dynamics

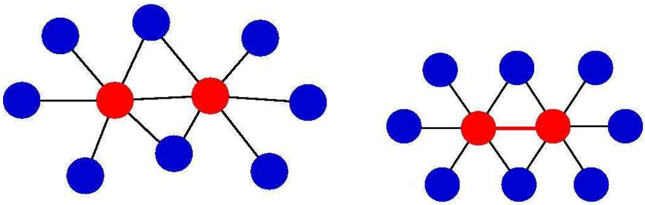
Diagram
neighboring boxes
Find the first collision for each particle
into the list
update first collision
update the list
next collision

Local crystal symmetry

Hard spheres system. $\rho = 1.03$

Loading

Local crystal symmetry



Definition of the order parameter

Observables for the Local Bond Ordering:

In 3d:

$$\bar{q}_{6m}(i) := \frac{1}{n(i)} \sum_{j=1}^{n(i)} Y_{6m}(\vec{r}_{ij}) \quad , r_{ij} < 1.4$$

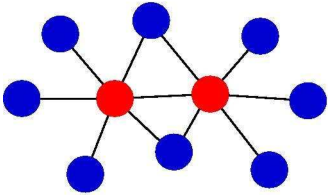
where $Y_{6m}(\vec{r}_{ij})$ *are the spherical harmonics (with l=6).*

Crystalline particles (colorcoded "green"), $n_b > 10$.

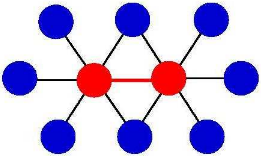
Low symmetry cluster (LSC)(colorcoded "light brown"), $n_b > 5$.

P. J. Steinhardt, D. R. Nelson, and M. Ronchetti. Phys. Rev. B, 28(2), 1983

Local crystal symmetry

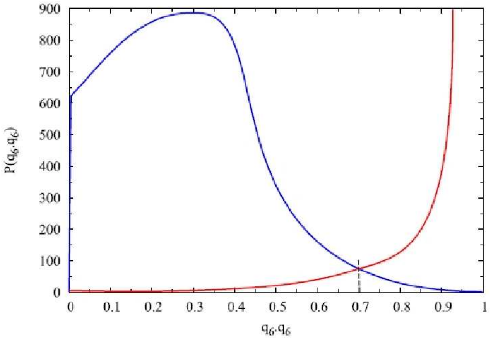


$\vec{q_6}(i) \cdot \vec{q_6^*}(j) < 0.7$



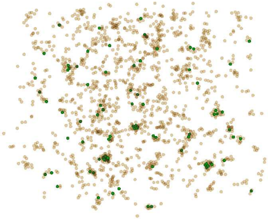
$\vec{q_6}(i) \cdot \vec{q_6^*}(j) > 0.7$

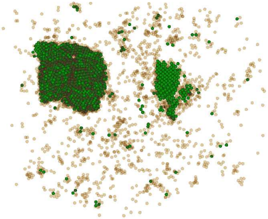
Distribution of the order parameter



source Hamed Maleki, PhD Thesis, University of Mainz, 2011

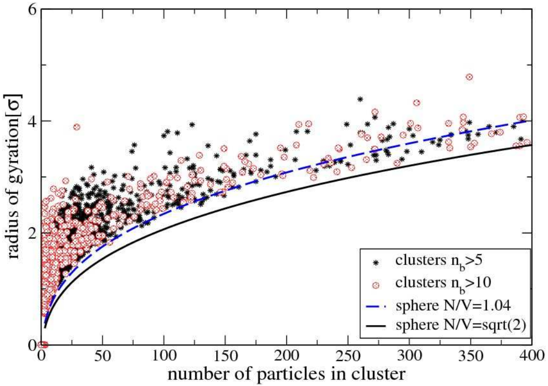
two snapshots





⇒ Spontaneous formation of a crystallite

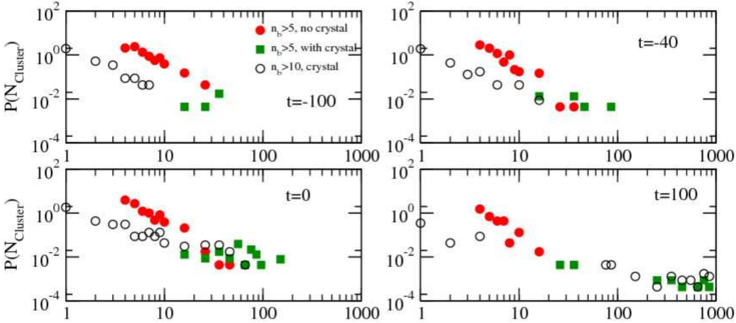
Radius of gyration



⇒ Small crystallites are far from being spherical

Schilling T.; Dorosz S.; Schoepe H. J.; et al. JPCM, 23, 19, 194120, 2011

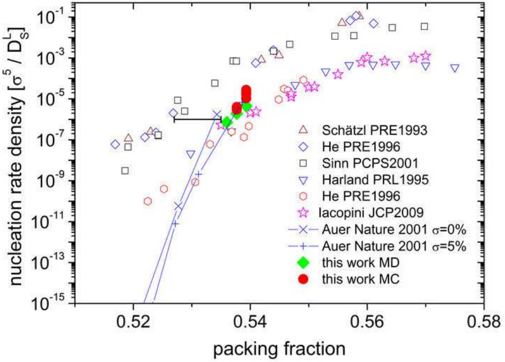
Precursor nucleation



$\Rightarrow$ Effective two step process. Precursor formation

Schilling T.; Dorosz S.; Schoepe H. J.; et al. JPCM, 23, 19, 194120, 2011

nucleation rates

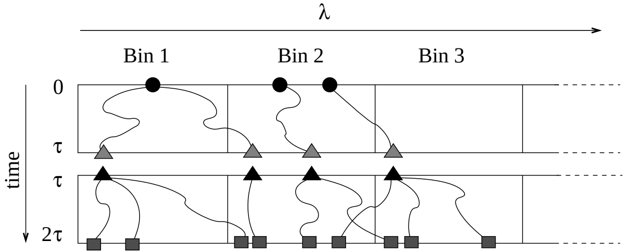


⇒ MD and MC simulations produce rates match the experimental results

⇒ SPRES as the first full non equilibrium rare event sampling method

Schilling T.; Dorosz S.; Schoepe H. J.; et al. JPCM, 23, 19, 194120, 2011

SPRES



J.T. Berryman and T. Schilling. Sampling rare events in nonequilibrium and nonstationary systems.

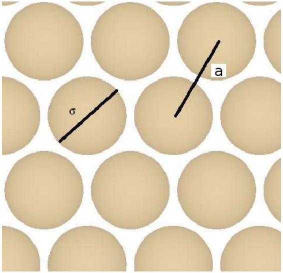
J Chem Phys, 133(24):244101, 2010.

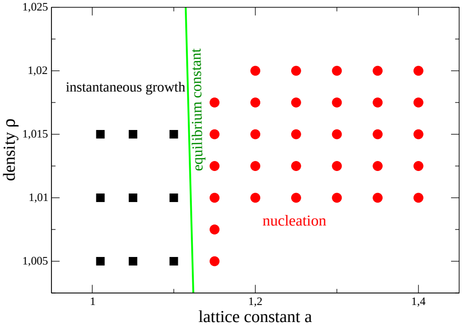
Motivation

- Will the substrate induce different nucleation pathways?
- Where does the nucleation happen?
- What are the consequences of the mismatch between substrate and equilibrium crystal lattice constant?
- What is the crystal structure of the nucleus?
- How does the substrate change the nucleation rate?

Setup of the system

We studied a super-saturated fluid of hard spheres in contact with a triangular substrate.



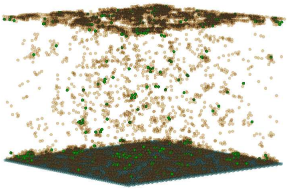


Parameters

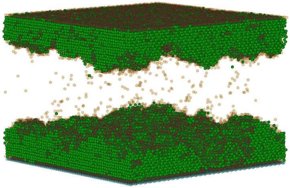
$N = 220200$ (216000 bulk + 4200 substrate) particles
$N\sigma^3/V = 1.005$ ($\eta = 0.526$) – 1.02 ($\eta = 0.534$)
Corresponding chemical potentials $-\Delta\mu \simeq 0.50 - 0.54\ k_B T$

Immediate wetting

$a < a_{eq}$

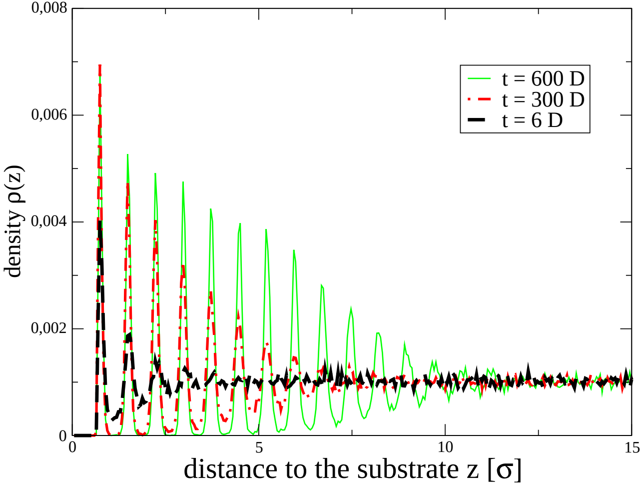


$t = 6D$



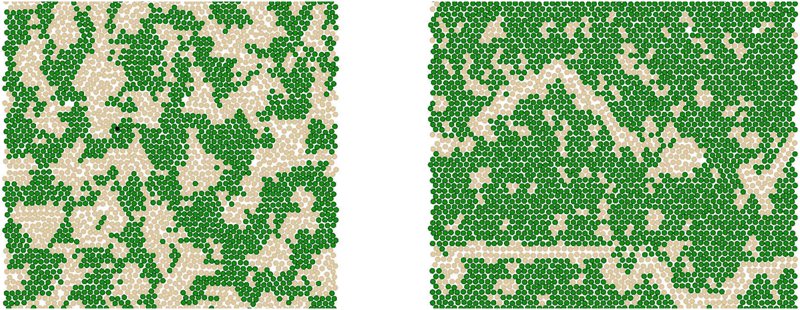
$t = 150D$

vertical density profile

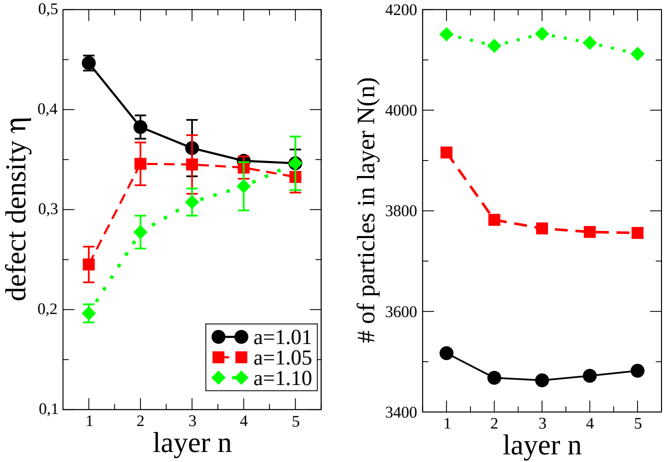


The first layer

at $t > 150D$

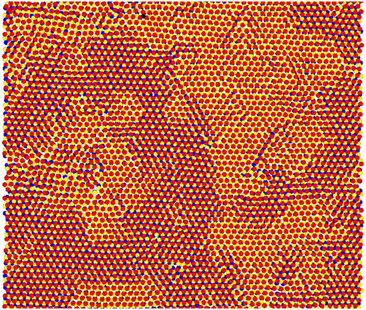


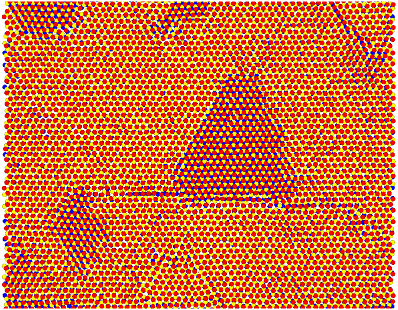
Defect density



⇒ Induced defects are compensated in the first 3 layers

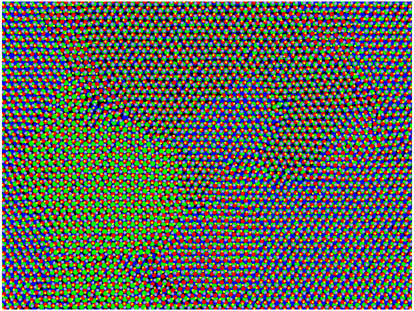
3 layer stacking

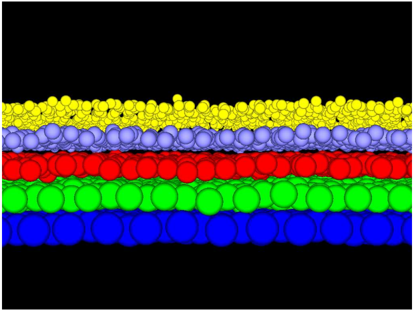




$\Rightarrow$ Domains of ABA and ABC structure

5 layer stacking

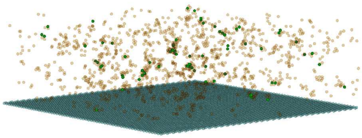




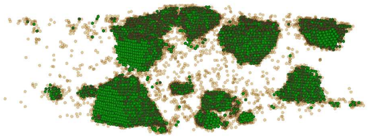
⇒ Crystal grows in random hexagonal closed packing (RHCP)

Nucleation at the wall

$a > a_{eq}$



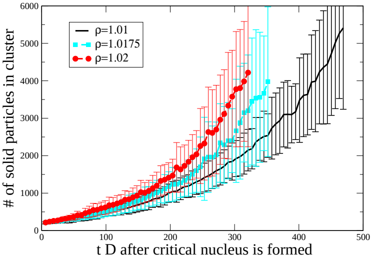
$t = 6D$

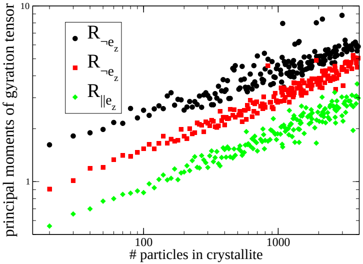


$t = 80D$

$\Rightarrow$ Droplet formation on the substrate

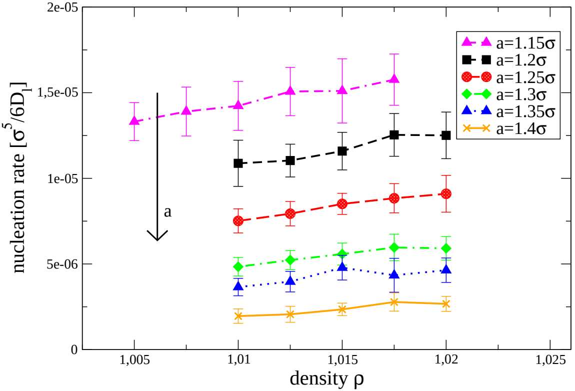
Droplet characterization





⇒ Analysis of the droplets shows non-spherical droplets even up to 4000 particles.

Nucleation rates



⇒ Decreasing nucleation rate with increasing mismatch to the substrate

Acknowledgements

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Group

J. Berryman, M. Anwar, M. Sinha, T. Schilling, S. Dorosz.

M. Radu missing.